

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19)



Eur päisches Patentamt
European Patent Office
Office uropéen des br v ts

(11) Publication number:

0 070 386
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82104992.1

(51) Int. Cl.³: **C 07 D 401/12, C 08 K 5/34,**
C 08 G 73/06

(22) Date of filing: 08.06.82

(30) Priority: 20.07.81 US 285240
20.07.81 US 285239

(71) Applicant: **AMERICAN CYANAMID COMPANY,**
1837 West Main Street P.O. Box 60, Stamford
Connecticut 06904 (US)

(43) Date of publication of application: 26.01.83
Bulletin 83/4

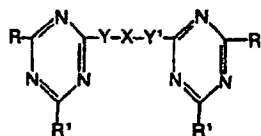
(72) Inventor: **Loffelman, Frank Fred, 1255 Cornell Road,**
Bridgewater New Jersey 08807 (US)
Inventor: **Brady, Thomas Eugene, 8 Dorset Lane,**
Whitehouse Station New Jersey 08889 (US)

(84) Designated Contracting States: AT BE CH DE FR GB IT
LI NL SE

(74) Representative: **Wächtershäuser, Günter, Dr., Tal 29,**
D-8000 München 2 (DE)

(64) Novel light stabilizers for polymers.

(57) Compounds of the formula



wherein R represents C₁-C₈ alkenyloxy, C₁-C₈ alkenylamino, or di(C₁-C₈ alkenyl)amino and wherein at least one of the groups contains a 4-piperidiny moiety, and polymers thereof as light stabilizers for polymers.

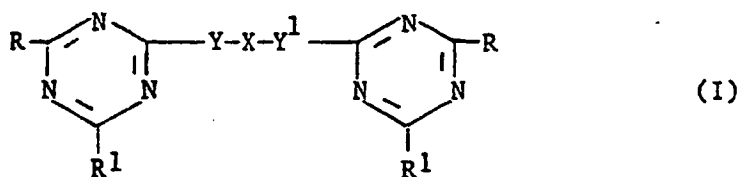
EP 0 070 386 A1

ACTORUM AG

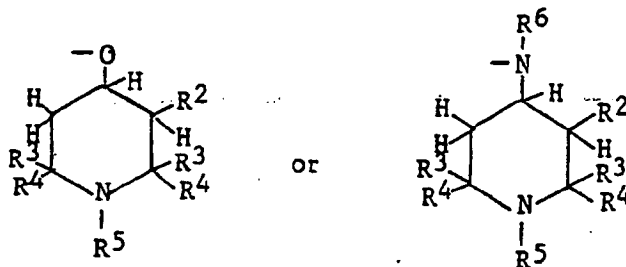
28,616

Novel Light Stabilizers for Polymers

This invention relates to certain novel compounds, polymers thereof and to their use as light stabilizers. More particularly, this invention relates to novel compounds of the formula (I)



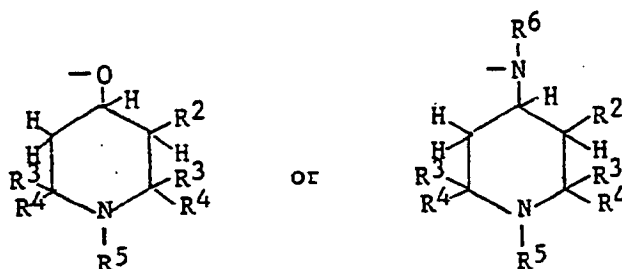
wherein R represents C₃-C₆ alkenyloxy, C₃-C₆ alkenylamino, or di(C₃-C₆ alkenyl)amino; R¹ represents C₁-C₈ alkyl, C₁-C₈ alkoxy, halo, C₁-C₈ alkylthio, C₃-C₆ alkenyloxy, amino, C₃-C₆ alkenylamino, di(C₃-C₆ alkenyl)amino, the groups



wherein R², R³, R⁴, R⁵, and R⁶ are as defined below, C₁-C₁₈ alkylamino, C₁-C₁₈ dialkylamino, morpholino, piperidino, pyrrolidyl, a substituted C₁-C₁₈ alkylamino, or a substituted C₁-C₁₈ dialkylamino, wherein the substituents

are selected from amino, cyano, carboxy, alkoxy carbonyl wherein the alkoxy moiety has 1 to 8 carbon atoms, and the groups

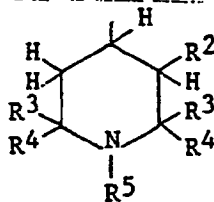
5



10

wherein R^2 represents hydrogen, C_1 - C_8 alkyl, or benzyl; R^3 and R^4 independently represent C_1 - C_8 alkyl, benzyl, or phenethyl, or together with the carbon to which they are attached form a C_5 - C_{10} cycloalkyl; and R^5 represents hydrogen, C_2 - C_3 hydroxyalkyl, C_1 - C_8 alkyl, hydroxyl, or oxyl; R^6 represents hydrogen, C_1 - C_8 alkyl, or

20

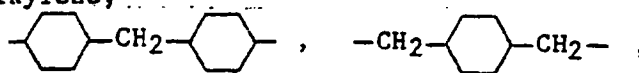


25

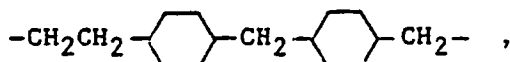
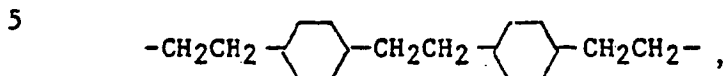
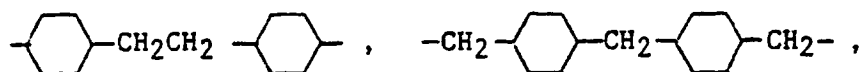
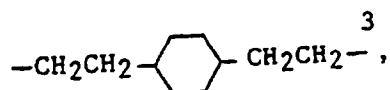
wherein R^2 , R^3 , R^4 , and R^5 are as previously defined; Y and Y', which may be the same, or different, represent

30

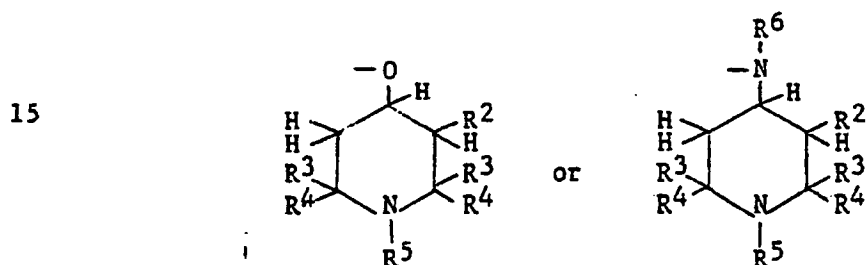
oxy, or $-N-$, wherein R^6 is as previously defined; X represents C_2 - C_{12} alkylene, wherein the alkylene chain may be interrupted by an oxy, thio, or $-N-$ radical, C_5 - C_{10} cycloalkylene,



35

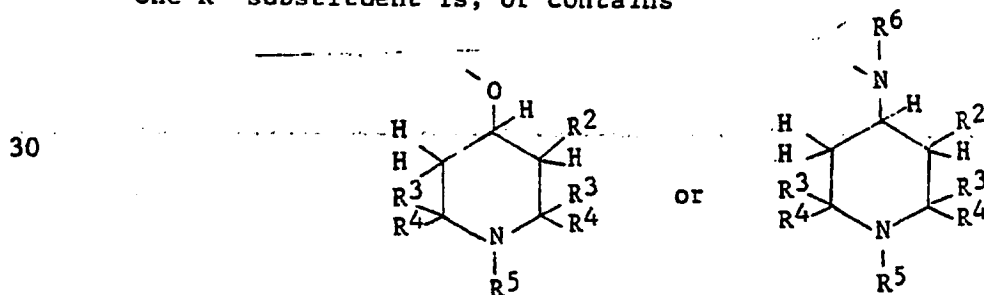


$\text{C}_6\text{-C}_{12}$ arylene, or $\text{C}_8\text{-C}_{14}$ aralkylene; with the proviso that when Y and Y' are oxy, or R^6 is hydrogen, or $\text{C}_1\text{-C}_8$ alkyl, at least one R^1 is, or contains,



and with the further proviso that R and R^1 are not allyloxy at the same time.

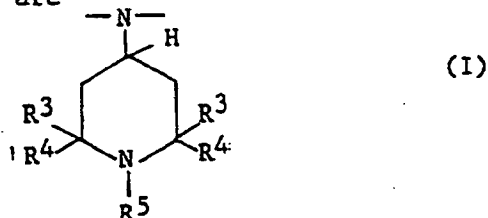
The invention further relates to polymeric compositions obtained by the polymerization, or copolymerization, of a monomer, or mixture of monomers, represented by formula I, above, with the only proviso being that at least one R^1 substituent is, or contains



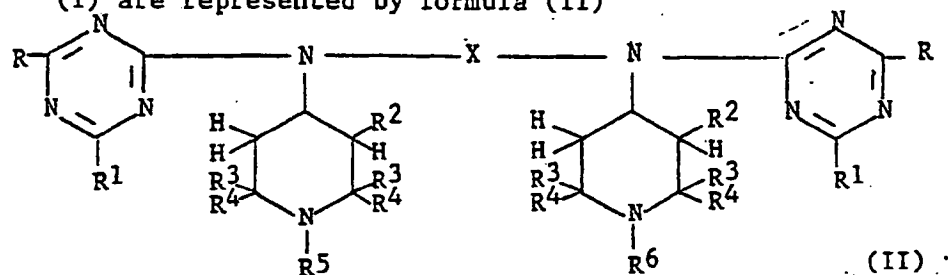
35

The invention also relates to the use of such compounds and/or polymeric compositions for stabilizing polymers, particularly polyolefins, against degradation by ultraviolet radiation, and to the stabilized compositions.

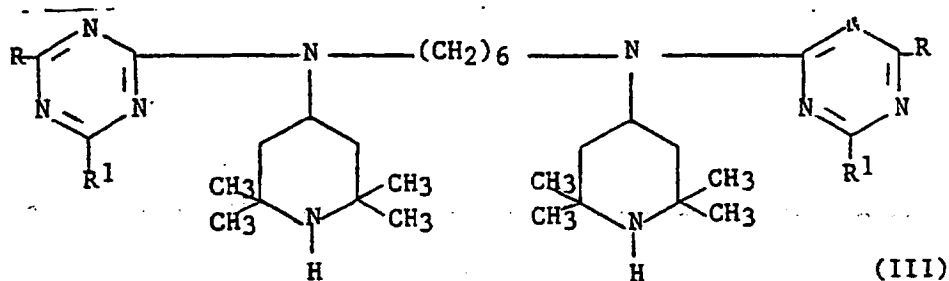
The preferred monomers of formula (I) are those wherein Y and Y' are



The especially preferred compounds of formula (I) are represented by formula (II)



The most especially preferred compounds are represented by formula (III)



It is well-known that sunlight and other sources of ultraviolet radiation cause degradation of polymers as evidenced by embrittlement or yellowing of plastic articles made therefrom. It is also well-known that this degradation can be inhibited by use of ultraviolet light stabilizers incorporated in or on such articles. Various additives, used alone or in combinations, have been suggested to

inhibit such light degradation in order to prolong the useful lives of articles made from polymers. Since none has been found to be completely satisfactory, research continues in order to find compounds, or combinations of compounds, which will be more satisfactory. The present invention arose out of such research and resulted in the discovery of novel compounds and polymers which stabilize polymers against degradation by ultraviolet light.

The stabilizers of the present invention offer the following advantages:

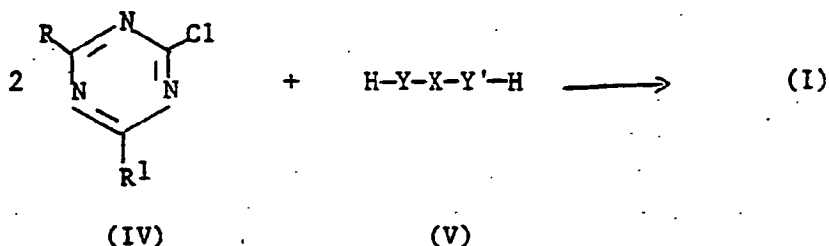
- (1) excellent light-stabilizing activity,
- (2) excellent compatibility with resins,
- (3) low volatility,
- (4) low extractability from polymers by laundering or dry cleaning, and
- (5) excellent oven-aging stability.

W. German Offen. 2,308,611 discloses bridged 1-3,5-triazines containing allyloxy, methallyloxy, or propallyloxy substituents.

Beyer and Lemke Chem. Ber. 99(7), 2123-6 (1966) disclose bridged 1,3,5-triazines containing methallyl substituents.

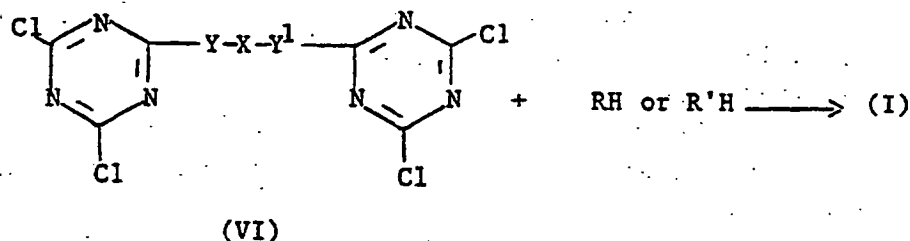
U. S. Patents 2,712,004 and 4,086,204 disclose respectively, the polymerization of allyl melamines and polytriazine compositions containing a tetraalkyl piperidine, as light stabilizers for polymers.

The compounds of formula (I) may be prepared by reacting two moles of an appropriately substituted chloro-1,3,5-triazine of formula (IV) with one mole of an appropriately substituted diol, or diamine, of formula (V), as illustrated by the following reaction, wherein R, R', X, Y, and Y' are as previously defined.



The preparation of suitable compounds of formulas (IV) and (V) is well-known in the art. The preparation of 4,4'-(hexamethylenediimino)bis(2,2,6,6-tetramethylpiperidine), also known as N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, is disclosed in U.S. Patent 4,104,248.

Some compounds of formula (I) may be prepared by reacting a compound of formula (VI) with an appropriate amine or alcohol, as shown below.



The compounds of Formula (VI) may be prepared from cyanuric chloride and an appropriate diol, or diamine, by conventional methods.

Illustrative examples of suitable compounds of formula (I) include the following:

2,2' [ethylenebis[2,2,6,6-tetramethyl-4-piperidinyl imido]] bis[4-allylamino-6-(2-cyanoethyl) amino-1,3,5-triazine],

2,2' -[hexamethylenebis[2,2,6,6-tetramethyl-4-piperidinyl imino]] bis(4-diallylamino-6-n-hexyl-1,3,5-triazine),

2,2' -[thiodiethylenebis[(2,2,6,6-tetraethyl-4-piperidinyl imino)] bis[4-allylamino-6-(2-aminoethyl) amino-1,3,5-triazine],

- 2,2'-[oxydihexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallyloxy-1,3,5-triazine),
- 5 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis[4-allyloxy-6-(2-carboxyethyl)amino-1,3,5-triazine],
- 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-diallylamino-6-t-octylamino-1,3,5-triazine),
- 10 2,2'-[tetramethylenebis[1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidinyl]imino]]bis(4,6-di-methallyloxy-1,3,5-triazine),
- 2,2'-[hexamethylenebis[(1-oxy-2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-(3-butenyl)amino-1,3,5-triazine),
- 15 2,2'-[hexamethylenebis[(1-hydroxy-2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallylamino-1,3,5-triazine),
- 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis-(4-diallylamino-6-methoxy-1,3,5-triazine),
- 20 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-allyloxy-6-diethylamino-1,3,5-triazine),
- 2,2'-[trimethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-allyloxy-6-n-butoxy-1,3,5-triazine),
- 25 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-dimethallyloxy-1,3,5-triazine),
- 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-chloro-6-dimethallylamino-1,3,5-triazine),
- 30 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-di(5-hexenyl)amino-1,3,5-triazine),
- 35 2,2'-(hexamethylenediimino)bis[4-allyloxy-6-(2,2,6,6-tetramethyl-4-piperidinyl)amino-1,3,5-triazine],

- 2,2'-(hexamethylenediimino)bis[4-methallyloxy-6-(2,2,6,6-tetraethyl-4-piperidiny)amino-1,3,5-triazine],
- 2,2'-(hexamethylenediimino)bis[4-methallyloxy-6-(2,2,6,6-tetramethyl-4-piperidinyloxy-1,3,5-triazine],
- 2,2'-[ethylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis[4,6-di(3-butenyl)-amino-1,3,5-triazine],
- 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis(4-allyloxy-6-ethylthio-1,3,5-triazine),
- 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis(4-allylamino-6-morpholino-1,3,5-triazine),
- 2,2'-[dodecamethylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis(4-diallylamino-6-piperidino-1,3,5-triazine),
- 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis(4-diallylamino-6-pyrrolidyl-1,3,5-triazine),
- 2,2'-[1,4-cyclohexylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis[4-diallylamino-6-(2-ethoxycarbonyl-ethylamino)-1,3,5-triazine],
- 2,2'-(hexamethylenediimino)bis[4-allyloxy-6-(2,2,3,6,6-pentamethyl-4-piperidiny)amino-1,3,5-triazine],
- 2,2'-[1,4-cyclohexylenebis(methylene)]bis[4-allylamino-6-(2-benzyl-2,6,6-trimethyl-4-piperidiny)amino-1,3,5-triazine],
- 2,2'-(hexamethylenediimino)bis[4-allylamino-6-(7-azadispiro[5.1.5.3]hexadecan-15-yl)-amino-1,3,5-triazine],
- 2,2'-[1,4-cyclohexylenebis(ethylene)]bis[4-allylamino-6-(2,2,6,6-tetramethyl-4-piperidiny)amino-1,3,5-triazine],
- 2,2'-[1,4-(phenylenedimethylene)bis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis(4,6-dimethallyloxy-1,3,5-triazine),

2,2'-[hexamethylenebis(methylimino)]bis-
[4-allylamino-6-(2,2,6,6-tetramethyl-4-
piperidinyl)amino-1,3,5-triazine],

2,2'-[hexamethylenebis(n-hexylimino)]bis-
[4-diallylamino-6-(2,2,6,6-tetramethyl-
4-piperidinyl)amino-1,3,5-triazine],

5 2,2'-(hexamethylenedioxy)bis[4-diallyl-
amino-6-(2,2,6,6-tetramethyl-4-piperi-
dinyl)amino-1,3,5-triazine],

2,2'-(ethylenedioxy)bis[4-allyloxy-6-
(2,2,6,6-tetramethyl-4-piperidinyl)amino-
1,3,5-triazine],

10 2,2'-(dodecamethylenedioxy)bis[4-diallyl-
amino-6-(2,2,6,6-tetramethyl-4-piperi-
dinyl)amino-1,3,5-triazine],

2,2'-(thiodiethylenedioxy)bis[4-diallyl-
amino-6-(2,2,6,6-tetramethyl-4-piperi-
dinyl)-oxy-1,3,5-triazine],

15 2,2'-[hexamethylenebis[(2-benzyl-2,6,6-
trimethyl-4-piperidinyl)imino]]bis-
(4,6-diallyloxy-1,3,5-triazine),

2,2'-[methylenedi-4,1-cyclohexylenebis[(2,2,-
6,6-tetramethyl-4-piperidinyl)imino]]bis-
20 (4-allylamino-6-t-octylamino-1,3,5-tri-
azine),

2,2'-[hexamethylenebis[(2,2,6,6-tetrameth-
yl-4-piperidinyl)imino]]bis(4-allylamino-
6-t-octylamino-1,3,5-triazine),

25 2,2'-[hexamethylenebis[(2,2,6,6-tetrameth-
yl-4-piperidinyl)imino]]bis(4,6-di-allyl-
amino-1,3,5-triazine),

2,2'-[ethylenebis[(2,2,6,6-tetramethyl-4-
piperidinyl)imino]]bis(4-allyloxy-6-t-
octylamino-1,3,5-triazine),

30 2,2'-[ethylenebis[(2,2,6,6-tetramethyl-4-
piperidinyl)imino]]bis(4,6-di-allylamino-
-1,3,5-triazine),

2,2'-(hexamethylenediimino)bis[4-allylamino-
6-[[6-[(2,2,6,6-tetramethyl-4-piperidinyl)-
amino]hexyl]amino]-1,3,5-triazine], and

35

2,2'-(hexamethylenediimino)bis[4-allyloxy-
-6-[[6-[(2,2,6,6-tetramethyl-4-piperidinyl)-
oxy]hexyl]amino]-1,3,5-triazine, and the
like.

5 In preparing the polymers of the present inven-
tion, a monomer of formula (I), or a mixture of a monomer
of formula (I) and any copolymerizable comonomer, is poly-
merized employing an effective amount of a polymerization
catalyst. Suitable polymerization catalysts include 2,2'-
azobisisobutyronitrile, di-(t-butyl)peroxide, dilaurylpe-
roxide, lauroyl peroxide, benzoyl peroxide, acetyl perox-
10 ide, t-butyl hydrogen peroxide, ammonium persulfate, pot-
assium persulfate, and the like. The preferred catalyst is
2,2'-azobisisobutyronitrile.

The monomer of formula (I) may be homopolymer-
ized, or copolymerized by utilizing a copolymerizable co-
15 monomer, in emulsion or solution by conventional methods.
Suitable comonomers are disclosed in U.S. Patent 2,712,004.

The compounds and polymers of this invention are
useful as light stabilizers for thermoplastic substrates
such as polyolefins, polyesters, polyethers, polyurethanes,
20 polystyrenes, high-impact polystyrenes, and the like. Pre-
ferably, the thermoplastic substrate is a polyolefin.

Other organic materials susceptible to degra-
dation by the effects of light, the properties of which are
improved by the incorporation therein of a compound of this
25 invention, include natural and synthetic rubbers; the lat-
ter include, for example, homo-, co- and terpolymers of
acrylonitrile, butadiene and styrene, and blends thereof.

The compounds of formula (I) and the polymers
thereof are particularly useful in polyolefins, such as
30 polyethylene, polypropylene, polybutylene, and the like,
and copolymers thereof.

Generally, the compositions comprise a polymer
containing from about 0.1% to about 5% by weight of the
compound of formula (I) or polymer thereof based on the
35 weight of the polymeric substrate.

Preferably, the composition comprises a polyolefin containing from about 0.2% to about 2% by weight of the compound of formula (I) or polymer thereof, based on the weight of the polyolefin substrate.

5 Optionally, the compositions may contain other additives, especially additives useful in polyolefins, such as antioxidants, supplemental light stabilizers, plasticizers, flame retardants, antistatic and antislipping agents, fillers, dyes, pigments, and the like.

10 Suitable antioxidants include those of the hindered phenol type, such as 2,6-di-t-butyl-p-cresol; 4,4'-bis(2,6-di-t-butylphenol); 4,4'-bis(2,6-diisopropylphenol); 2,4,6-tri-t-butylphenol; 2,2'-thiobis(4-methyl-6-t-butylphenol); octadecyl 2(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-2,4,6-(1H,3H,5H)-trione; esters of thiodipropionic acid, such as dilauryl thiodipropionate and distearyl thiodipropionate, etc; hydrocarbyl phosphites, such as triphenyl phosphite, trinonyl phosphite, diisodecyl pentaerythrityl diphosphite, diphenyldecyl phosphite, etc; and combinations thereof.

15 20

25 Suitable supplemental light stabilizers include those of the benzotriazole class, such as 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole; 2-(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chlorobenzotriazole; those of the hydroxybenzophenone type, such as 2-hydroxy-4-methoxybenzophenone; 2-hydroxy-4-octyloxybenzophenone; 2,2'-dihydroxy-4,4'-dimethoxybenzophenone; hindered phenol esters, such as n-hexadecyl 3,5-di-t-butyl-4-hydroxybenzoate, and 2',4'-di-t-butylphenyl 3,5-di-t-butyl-4-hydroxybenzoate; metal complexes, such as nickel complexes of 2,2'-thiobis(4-t-octylphenol); nickel butylamine complex of 2,2'-thiobis(4-t-octylphenol); nickel complexes of bis(4-t-octylphenyl)sulfone; nickel dibutyl dithiocarbamate; nickel salts of 4-hydroxy-3,5-di-t-butylbenzyl phosphonic acid monoalkyl esters where alkyl is methyl, ethyl, propyl, butyl, etc;

30 35

nickel complex of 2-hydroxy-4-methylphenyl undecyl ketone oxime, etc. Further illustrative examples of suitable antioxidants and supplemental light stabilizers can be found in columns 3 and 4 of U.S. Patents 3,488,290 and 3,496,134 and in the other patents mentioned therein.

5 As with the compound of formula (I) and polymers thereof, the additive is advantageously employed within the range from about 0.2% to about 2% by weight, based on the weight of the untreated polymer.

10 The compound of formula (I) and polymers thereof may be incorporated into the polymeric substrate by any of the known techniques for compounding additives with a polymer. For example, the polymer or compound may be compounded by dry blending with the polymer substrate in powder or granular form, followed by milling, Banbury mixing, molding, casting, extruding, swelling, and the like. 15 Alternatively, the additive may be added, as a solution or slurry in a suitable inert solvent, or dispersant, to the polymeric substrate in powder or granular form, the whole mixed intimately in a mixer, and the solvent subsequently removed. As a further possibility, the additive may be added 20 to the polymeric substrate during the preparation of the latter, for instance at the latex stage of polymer production, to provide prestabilized polymer material.

25 The following examples illustrate the present invention. All parts and percentages are by weight unless otherwise indicated.

Example 1

30 Preparation of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallylamino-1,3,5-triazine)

35 A mixture of 2,4-bis(diallylamino)-6-chloro-1,3,5-triazine (14.2 grams; 0.046 mole), 4,4'-(hexamethylenediimino)bis(2,2,6,6-tetramethylpiperidine) (9.2 grams; 0.023 mole), powdered sodium hydroxide (1.84 grams; 0.046 mole), and xylene (50 mls) is heated at reflux for 36 hours using a water separator to remove byproduct water. The

reaction mixture is then filtered hot and the filtrate is evaporated to obtain a light yellow oil which solidifies on standing. Recrystallization of the solid from hexane gives white needles which on recovery and drying weigh 9.3 grams, mp 119-120°C.

- 5 Calculated for $C_{54}H_{88}N_{14}$: C, 69.53%; H, 9.44%; N, 21.03%
 Found: C, 69.45%; H, 9.44%; N, 20.86%

Example 2

- 10 Preparation of 2,2'-[Hexamethylenebis[(2,2,6,6-tetra-
 methyl-4-piperidinyl)imino]]bis(4-diallylamino-6-meth-
 oxy-1,3,5-triazine)

- 15 A mixture of 2-diallylamino-4-chloro-6-methoxy-1,3,5-triazine (21.6 grams; 0.09 mole), 4,4'-(hexamethylenediimino)bis(2,2,6,6-tetramethylpiperidine) (17.9 grams; 0.045 mole), powdered sodium hydroxide (3.6 grams; 0.09 mole), and xylene (150 mls) is heated at reflux for 24 hours using a water separator to remove water therefrom. The reaction mixture is then processed as described in Example 1 to obtain 21.3 grams of crystalline product, mp 113°C-115°C.

- 20 Calculated for $C_{44}H_{74}N_{12}O_2$: C, 65.82%; H, 9.23%; N, 20.95%
 Found: C, 65.61%; H, 8.95%; N, 21.12%

Example 3

- 25 Preparation of 2,2'-[Hexamethylenebis[(2,2,6,6-tetra-
 methyl-4-piperidinyl)imino]]bis(4-diallylamino-6-t-
 octylamino-1,3,5-triazine)

- 30 A stirred solution of 4,4'-(hexamethylenediimino)bis(2,2,6,6-tetramethylpiperidine) (9.5 grams; 0.024 mole), 2-diallylamino-4-chloro-6-t-octylamino-1,3,5-triazine (16.0 grams; 0.048 mole), and powdered sodium hydroxide (2.0 grams; 0.05 mole) in xylene (150 mls) is heated at reflux for 24 hours while removing by-product water by means of a trap. The resulting mixture is then filtered and the filtrate is heated to evaporate the solvent and obtain a light tan oil which solidifies on triturating with petroleum ether. The solid is then recovered and dried to obtain 4.6 grams of the desired product, mp 113-115°C.

Calculated for $C_{58}H_{104}N_{14}$: C, 69.87%; H, 10.44%; N, 19.68%

Found: C, 69.70%; H, 11.02%; N, 19.78%

Example 4

Preparation of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-allyloxy-6-t-octyl-amino-1,3,5-triazine)

5 A stirred mixture of 4,4'-(hexamethylenediimino)-bis(2,2,6,6-tetramethylpiperidine) (10.0 grams; 0.025 mole), 2-allyloxy-4-chloro-6-t-octylamino-1,3,5-triazine (15.1 grams; 0.05 mole), and powdered sodium hydroxide (2.0 grams; 10 0.05 mole) in xylene (150 mls) is heated at reflux for 24 hours while removing by-product water by means of a trap. The reaction mixture is filtered while hot to remove insolubles. Upon cooling the filtrate, a white crystalline solid precipitates. The solid is recovered by filtration 15 and dried to obtain 15.7 grams of the desired product, mp 210-212°C.

Calculated for $C_{52}H_{92}N_{12}O_2$: C, 68.12%; H, 10.04%; N, 18.34%

Found: C, 68.56%; H, 10.83%; N, 17.75%

Example 5

20 Preparation of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-allylamino-6-t-octyl-amino-1,3,5-triazine)

A stirred mixture of 4,4'-(hexamethylenediimino)-bis(2,2,6,6-tetramethylpiperidine) (8.0 grams; 0.0202 25 mole) in xylene (75 mls) is heated at reflux for 2 hours while removing water therein by means of a water trap. Powdered sodium hydroxide (1.62 grams; 0.0404 mole) and 2,4-di-allylamino-6-chloro-1,3,5-triazine (9.1 grams; 0.0404 mole) are added to the xylene and stirring and heating at 30 reflux is continued for 18 hours. The reaction mixture is then cooled to 25°C, and acetonitrile (200 mls) and water (50 mls) are added. The mixture is then stirred and heated at reflux for one hour, cooled to 25°C, and allowed to settle. The aqueous phase is then separated and the organic phase is 35 washed with water. The aqueous phase is separated again and the organic phase is dried over anhydrous sodium sulfate.

The mixture is filtered and the filtrate is concentrated to about 50 mls. On standing crystals are deposited which after recovery, rinsing with diethyl ether and drying weigh 8.2 grams, mp 160-162°C. Recrystallization from xylene gives a melting point of 161-162°C.

5 Calculated for $C_{42}H_{72}N_{14}$: C, 65.24%; H, 9.39%; N, 25.37%
 Found: C, 65.83%; H, 9.40%; N, 24.76%

Example 6

10 Preparation of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidiny)imino]]bis(4,6-di-allylamino-1,3,5-triazine)

 A stirred mixture of 4,4'-(hexamethylenediimino)-bis(2,2,6,6-tetramethylpiperidine) (6.36 grams; 0.0161 mole), 2-chloro-4,6-bis(t-octylamino)-1,3,5-triazine (9.56 grams; 0.0322 mole), and powdered sodium hydroxide (1.29 grams; 0.0322 mole) in xylene (75 mls) is stirred and heated at reflux while removing water therein by means of a water trap. The reaction mixture is stirred and heated at reflux for 18 hours, cooled to 25°C, and treated with acetonitrile (200 mls). The reaction mixture is filtered to recover a precipitate, and the solid is washed successively with water and acetone, and dried to obtain 10.0 grams of product which melts at 208-209°C after recrystallization from xylene.

25 Calculated for $C_{52}H_{94}N_{14}$: C, 68.22%; H, 10.35%; N, 21.43%
 Found: C, 69.11%; H, 10.48%; N, 19.81%

Examples 7-10

Testing in Polypropylene

30 The compounds of Examples 1-4 (0.25 gram) are separately dry blended with a mastermix of 100 grams of unstabilized polypropylene (Pro-fax® 6401) and 0.1 gram of a processing antioxidant, 2,4,6-tri-t-butylphenol. The blend is milled at 350-370°F for five minutes, and then compression molded at 400°F into a film 4-5 mils thick. The film and a control film, identically prepared without the compound under test, are exposed to a xenon arc in an Atlas

35

Weather-Ometer® until they fail. A film is considered as having failed when the carbonyl content of the infrared absorption spectrum increases by 0.10weight percent, a generally accepted point of film embrittlement.

5 The data in Table I show the number of hours required to increase the carbonyl content by 0.1% by weight for the compounds under test and a control film.

10

15

20

25

30

35

TABLE I

<u>Example</u>	<u>Additive</u>	<u>Hours to Failure</u>
7	Product of Example 1	1600
8	Product of Example 2	>1200
9	Product of Example 3	>900
10	Product of Example 4	>700
	None	<200

5

10

15

20

Example 11

Polymer of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallylamino-1,3,5-triazine)

Dry dioxane (13 grams) is purged with nitrogen for 45 minutes, and 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallylamino-1,3,5-triazine) (9.5 grams) is added thereto. The mixture is purged with nitrogen for an additional 35 minutes, and the nitrogen stream is then directed above the surface of the mixture. The temperature is raised to dissolve the crystals and then 2,2'-azobisisobutyronitrile (0.42 gram) is added to the solution. The temperature is raised to 65°C and held there for 24 hours while stirring and passing nitrogen over the surface of the reaction mixture. The gel-like insoluble material is recovered by filtration, stirred in petroleum ether, recovered again by filtration and dried to obtain 3.5 grams of polymer which does not melt at up to 300°C.

Example 12

Polymer of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallyloxy-1,3,5-triazine)

A mixture of 2,2'-[hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4,6-diallyloxy-1,3,5-triazine) (8.0 grams) and dioxane (15 mls) is purged with nitrogen for 30 minutes and 2,2'-azobisisobutyronitrile (1.0 gram) is added thereto. The reaction mixture is stirred and heated at 60°C for 68 hours while passing a stream of nitrogen above the surface of the mixture. An additional 0.5 gram of 2,2'-azobisisobutyronitrile is then added to the mixture and heating is continued at 60°C for 24 hours. An additional 0.5 gram of 2,2'-azobisisobutyronitrile is added to the mixture and heating is continued at 60°C for another 24 hours. The reaction mixture is then poured into petroleum ether (200 mls) and the resultant solid is recovered by filtration and dried in a vacuum oven. The product softens at 120°C and decomposes at 156-160°C. It has a molecular weight of 3000.

Example 13

Polymer of 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-diallylamino-6-methoxy-1,3,5-triazine)

5 2,2'-[Hexamethylenebis[(2,2,6,6-tetramethyl-4-piperidinyl)imino]]bis(4-diallylamino-6-methoxy-1,3,5-triazine) (10 grams) is dissolved in dry dioxane (15 grams) at 40°C and the solution is purged with dry nitrogen for 30 minutes. The solution is heated to 60°C, under a nitrogen atmosphere, and 2,2'-azobisisobutyronitrile (0.5 gram) is
10 added thereto. The reaction mixture is then stirred at 60°C for 24 hours. At this point, additional 2,2'-azobisisobutyronitrile (0.25 gram) is added to the reaction mixture and stirring is continued at 60°C for another 24 hours. An
15 additional 0.25 gram of 2,2'-azobisisobutyronitrile is added and stirring is continued at 60°C for another 24 hours. The reaction mixture is then added to petroleum ether (200 mls) and the resulting white precipitate is recovered by filtration and dried under vacuum to obtain 5.6 grams of
20 product which softens at 110°C and effervesces at 160-170°C.

Examples 14-16Testing in Polypropylene

The compounds of Examples 11-13 (0.25 gram) are separately dry blended with a mastermix of 100 grams of
25 unstabilized polypropylene (Pro-fax® 6401) and 0.1 gram of a processing antioxidant, 2,4,6-tri-t-butylphenol. The blend is milled at 350-370°F for five minutes, and then compression molded at 400°F into a film 4-5 mils thick. The film and a control film, identically prepared without the
30 compound under test, are exposed to a xenon arc in an Atlas Weather-Ometer® until they fail. A film is considered as having failed when the carbonyl content of the infrared absorption spectrum increases by 0.10 weight percent, a generally accepted point of film embrittlement.

35 The data in Table II show the number of hours required to increase the carbonyl content by 0.1% by weight for the compounds under test and a control film.

TABLE II

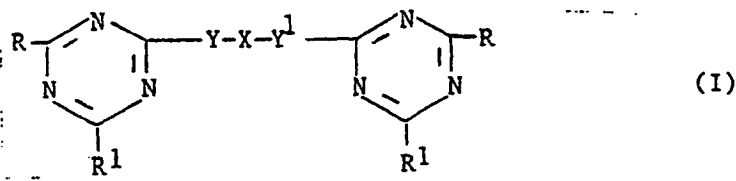
<u>Example</u>	<u>Additive</u>	<u>Hours to Failure</u>
14	Product of Example 11	300
15	Product of Example 12	400
16	Product of Example 13	600
	None	<200

-20-

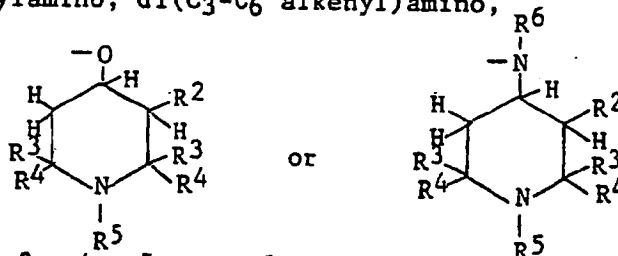
0070386

WHAT IS CLAIMED IS:

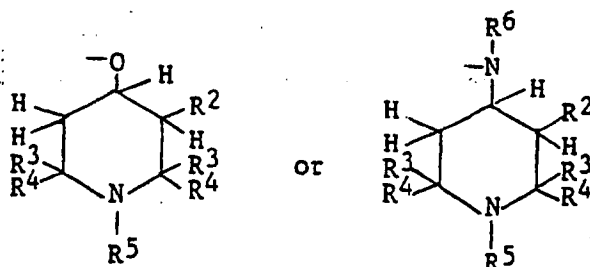
1. A compound of the formula (I)



wherein R represents C₃-C₆ alkenyloxy, C₃-C₆ alkenylamino, or di(C₃-C₆ alkenyl)amino; R¹ represents C₁-C₈ alkyl, C₁-C₈ alkoxy, halo, C₁-C₈ alkylthio, C₃-C₆ alkenyloxy, amino, C₃-C₆ alkenylamino, di(C₃-C₆ alkenyl)amino,

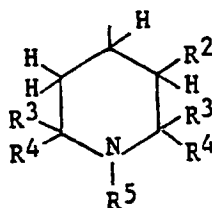


wherein R², R³, R⁴, R⁵, and R⁶ are as defined below, C₁-C₁₈ alkylamino, C₁-C₁₈ dialkylamino, morpholino, piperidino, pyrrolidyl, a substituted C₁-C₁₈ alkylamino, or a substituted C₁-C₁₈ dialkylamino, wherein the substituents are selected from amino, cyano, carboxy, alkoxy, carbonyl wherein the alkoxy moiety has 1 to 8 carbon atoms, and the groups



wherein R² represents hydrogen, C₁-C₈ alkyl, or benzyl; R³ and R⁴ independently represent C₁-C₈ alkyl, benzyl, or

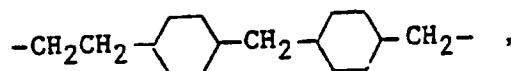
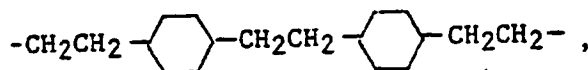
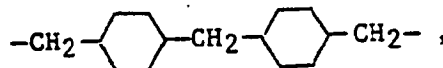
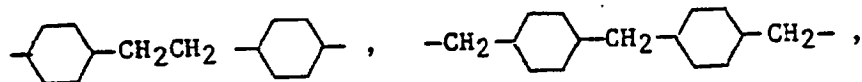
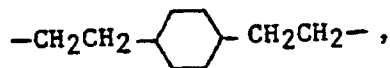
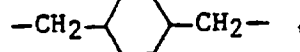
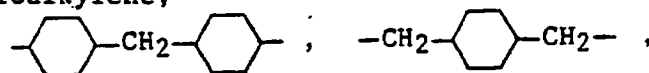
phenethyl, or together with the carbon to which they are attached form a C₅-C₁₀ cycloalkyl; and R⁵ represents hydrogen, C₂-C₃ hydroxyalkyl, C₁-C₈ alkyl, hydroxyl, or oxyl; R⁶ represents hydrogen, C₁-C₈ alkyl, or



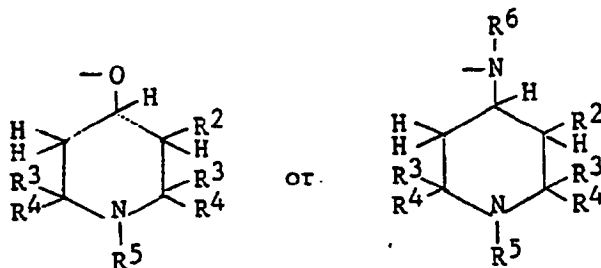
wherein R², R³, R⁴, and R⁵ are as previously defined; Y and Y¹, which may be the same, or different, represent

oxy, or -N-, wherein R⁶ is as previously defined; X represents C₂-C₁₂ alkylene, wherein the alkylene chain

may be interrupted by an oxy, thio, or -N- radical, C₅-C₁₀ cycloalkylene,

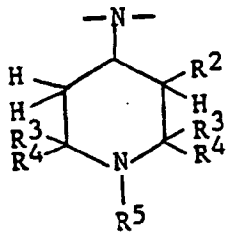


C₆-C₁₂ arylene, or C₈-C₁₄ aralkylene; with the proviso that when Y and Y' are oxy, or R⁶ is hydrogen, or C₁-C₈ alkyl, at least one R¹ is, or contains

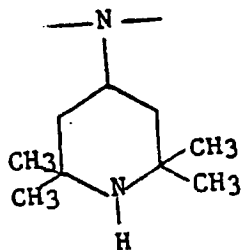


and with the further proviso that R and R¹ are not allyloxy at the same time.

2. The compound of Claim 1 wherein Y and Y¹ are each



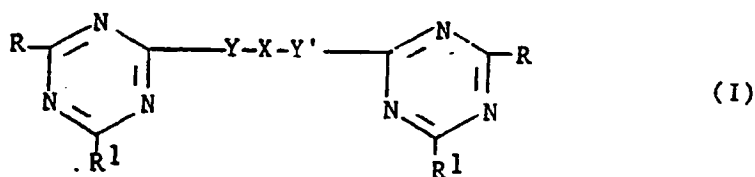
3. The compound of Claim 1 wherein X is (CH₂)₆ and Y and Y¹ are each



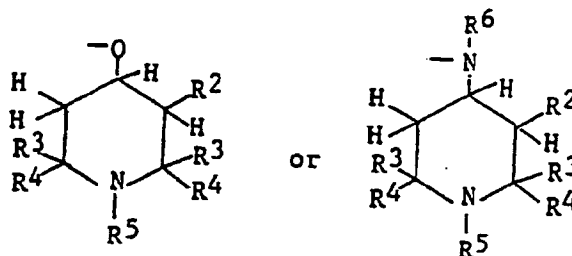
4. A method of stabilizing a polymer which is normally subject to degradation by ultraviolet radiation which comprises incorporating into said polymer an ultraviolet radiation stabilizingly effective amount of a stabilizer of Claim 1.

5. The method of Claim 11 wherein the polymer is a polyolefin.

6. A polymer prepared by polymerizing, optionally with a comonomer, a compound of the formula (I)

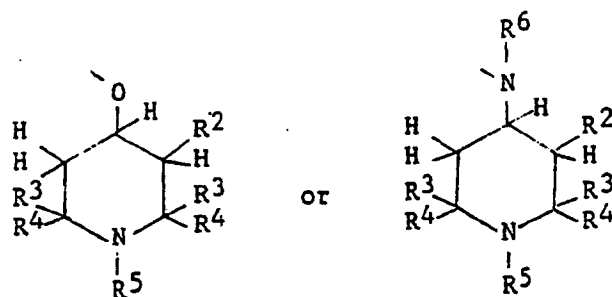


wherein R represents C₃-C₆ alkenyloxy, C₃-C₆ alkenylamino, or di(C₃-C₆ alkenyl)amino; R¹ represents C₁-C₈ alkyl, C₁-C₈ alkoxy, halo, C₁-C₈ alkylthio, C₃-C₆ alkenyloxy, amino, C₃-C₆ alkenylamino, di(C₃-C₆ alkenyl)amino, the groups

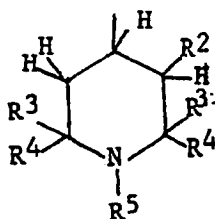


wherein R², R³, R⁴, R⁵, and R⁶ are as defined below, C₁-C₁₈ alkylamino, di(C₁-C₁₈)alkylamino, morpholino, pyrrolidyl, piperidino, a substituted C₁-C₁₈ alkylamino, or a substituted di(C₁-C₁₈)alkylamino, wherein the substituents are selected from amino, cyano, carboxy, alkoxy, carbonyl wherein the alkoxy moiety has 1 to 8 carbon atoms, and the groups

-25-



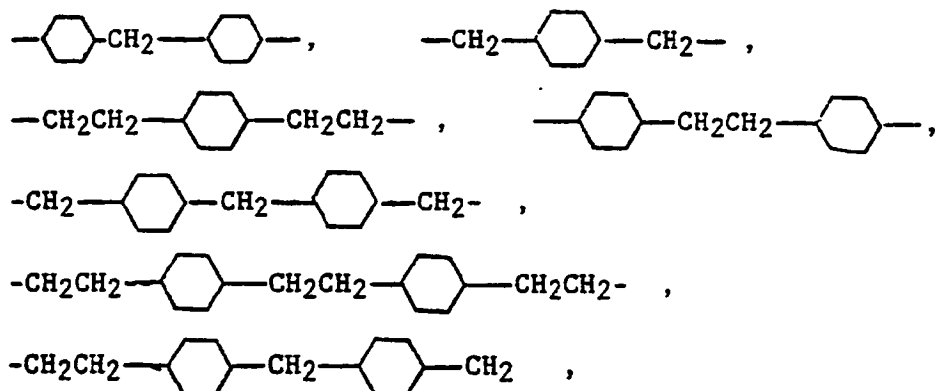
wherein R^2 represents hydrogen, C_1 - C_8 alkyl, or benzyl; R^3 and R^4 independently represent C_1 - C_8 alkyl, benzyl, or phenethyl, or together with the carbon to which they are attached form a C_5 - C_{10} cycloalkyl; and R^5 represents hydrogen, C_2 - C_3 hydroxyalkyl, C_1 - C_8 alkyl, hydroxyl, or oxyl; R^6 represents hydrogen, C_1 - C_8 alkyl, or



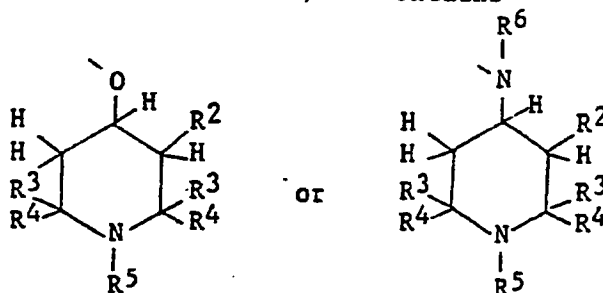
wherein R^2 , R^3 , R^4 , and R^5 are as previously defined; Y and Y', which may be the same, or different, represent

oxy, or $\text{--}\overset{\text{R}^6}{\text{N}}\text{--}$, wherein R^6 is as previously defined; X represents C_2 - C_{12} alkylene, wherein the alkylene chain may

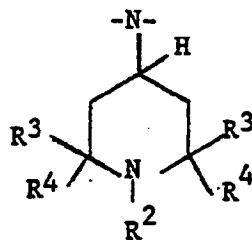
R^6
|
be interrupted by an oxy, thio, or $\text{--}\text{N--}$ radical C_5 - C_{10}
cycloalkylene,



C₆-C₁₂ arylene, or C₈-C₁₄ aralkylene; with the proviso that at least one R¹ substituent is, or contains



7. The polymer of Claim wherein Y and Y' are each



8. The polymer of Claim 7 wherein R³ and R⁴ are each methyl, R⁵ is hydrogen, and X is C₂-C₁₂ alkylene.

0070386

- 27 -

9. A method for stabilizing a polymer which is normally subject to degradation by ultraviolet radiation which comprises incorporating into said polymer an ultraviolet stabilizingly effective amount of a polymer of Claim 6.

10. The method of Claim 9 wherein the polymer to be stabilized is a polyolefin.

0070386



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 82 10 4992

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
D,Y	<p>--- DE-A-2 308 611 (SIEMENS AG.) * pages 1,2 *</p>	1	<p>C 07 D 401/12 C 08 K 5/34 C 08 G 73/06</p>
Y	<p>--- US-A-4 234 728 (CIBA-GEIGY) * column 1, lines 34-38; column 9, lines 11-15 *</p>	1,9	
A	<p>--- EP-A-0 013 682 (CIBA-GEIGY AG.) * claims *</p>	1,9	
A	<p>--- US-A-2 712 004 (AMERICAN CYNANAMIT COMP.) * page 1 *</p>		
A	<p>--- DE-B-1 302 636 (J.R. GEIGY AG.) * example 20 *</p> <p>-----</p>	1	<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 7)</p> <p>C 07 D 401/00</p>
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10-09-1982	Examiner VAN BIJLEN H.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

EPO Form 1503, 03/82